

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau

1911,072

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 25/02, 25/22	A1	(11) International Publication Number: WO 98/49 (43) International Publication Date: 12 November 1998 (12.1
 (21) International Application Number: PCT/US (22) International Filing Date: 19 March 1998 ((30) Priority Data: 08/850,792 2 May 1997 (02.05.97) (71) Applicant: ISP INVESTMENTS INC. [US/US]; 818 ton Street, Wilmington, DE 19801 (US). (72) Inventors: NARAYANAN, Kolazi, S.; 33 Carol Place NJ 07470 (US). JON, Domingo; Apartment 2 Kenmare Street, New York, NY 10012 (US). IAN Robert, M.; 5330 Berkshire Valley Road, Oak R07438 (US). (74) Agents: MAUE, Marilyn, J. et al.; International Products, Legal Dept., Building 10, 1361 Algebra, NJ 07470 (US). 	Washin e, Wayr 8, 41- NIELL Ridge, 1	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB GH, GM, GW, HU, ID, IL, IS, IP, KE, KG, KP, KR LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SI TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO p (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian p (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European p (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: SOLID DELIVERY SYSTEM (SDS) FOR ACTIVE AGRICULTURAL CHEMICALS

(57) Abstract

This invention relates to a solid delivery system (SDS) for active agricultural chemicals, and, more particularly, to a bioenhanced, stable SDS for sulfonyl and sulfamoylurea agricultural chemicals capable of forming aqueous microdispersions or tank mixes thereof suitable for application to a plant site.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM AT AU AZ BA BB	Armenia Austria Australia Azerbaijan	FI FR GA	Finland France	LT LU	Lithuania	SK	Slovakia
AU AZ BA BB	Australia		France	LU	*		
AZ BA BB		GA			Luxembourg	SN	Senegal
BA BB	Azerbaijan		Gabon	LV	Latvia	SZ	Swaziland
BB		GB	United Kingdom	MC	Monaco	TD	Chad
	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	· UZ	Uzbekistan
CF	Central African Republic	JР	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
СН	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	ΚZ	Kazakstan	RO	Romania		_
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

1

SOLID DELIVERY SYSTEM (SDS) FOR ACTIVE AGRICULTURAL CHEMICALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a solid delivery system (SDS) for active agricultural chemicals, and, more particularly, to a bioenhanced, stable SDS for sulfonyl and sulfamoylurea agricultural chemicals capable of forming aqueous microdispersions or tank mixes thereof suitable for application to a plant site.

2. Description of the Prior Art

Sulfonyl and sulfamoylurea (SU) herbicides are very susceptible to hydrolysis in water or in admixture with other polar organic solvents which promote proton exchange between such chemicals and the solvent. Particularly, both the sulfonyl and sulfamoylurea compounds have a labile sulfonamide bridge which decomposes readily in water. Accordingly, stabilized liquid emulsifiable concentrates of such herbicides have been developed which when added to water to form a tank mix are suitable for application to a plant site. Such liquid emulsifiable concentrates are described by Narayanan et al. in copending U.S. patent application Serial No. 08/733,285, filed October 17, 1996.

WO 98/49894 PCT/US98/05407

2

Narayanan, in U.S. Pat. 5,389,297, also has described an inert matrix composition in the form of a free-flowing, high melting solid suitable for making a microemulsifiable concentrate by slurrying the active with a small amount of water, and freeze-drying. This concentrate will provide an aqueous microemulsion upon dilution with tank mix water. However, for sulfonyl and sulfamoyl ureas, as described in this invention, it is more advantageous to keep these actives and water apart until the final application step, so as to minimize the hydrolysis effect on such actives, while maximizing the bioenhancing capability of the N-octyl pyrrolidone component of the inert matrix composition on these actives.

SUMMARY OF THE INVENTION

What is described herein is a bioenhanced, stable solid carrier system for one or more sulfonyl or sulfamoyl urea agricultural chemicals suitable for forming an aqueous microdispersed tank mix upon dilution with water, which comprises, by weight, (a) 80-99.5% of an inert matrix composition comprising 10-50% of a C_6-C_{18} alkyl pyrrolidone, about 5-50% of an anionic surfactant and about 10-70% of a water-soluble, high melting organic compound containing a dissociable proton which can complex with said pyrrolidone, a melting point of > 100°C. a molecular weight of ≤ 500 , and a water solubility of at least 10%, which is selected from the group consisting of hydroxy acids, amino acids, sugars and amides, and (b) 1-20% of said agricultural chemical, optionally with a diluent agricultural chemical.

WO 98/49894 PCT/US98/05407

3

A further feature of the invention is an aqueous dispersion tank mix comprising dilution water in an amount sufficient to reduce the concentration of the agriculturally active ingredient to between a few ppm and 1% by weight.

Still another aspect of the invention is a method of making such systems which comprises admixture (a) and (b) as separate components.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, the SDS includes (a) an inert matrix composition which comprises a higher lactam, i.e. a C_6 - C_{18} alkylpyrrolidone, e.g. N-octylpyrrolidone, N-isooctylpyrrolidone or N-dodecylpyrrolidone, or mixtures thereof. N-octylpyrrolidone is preferred. The lactam is present in an amount of about 10-50%, preferably 15-40%, and most preferably, 20-30%, by weight.

The second component is an anionic surfactant which is typified by an alkali metal salt of a C₈-C₂₂ aliphatic surfactant such as sodium dodecyl sulfate, or an alkyl aromatic sulfate, or sulfonates, ethoxylated derivatives of the above, alkylphenyl ethoxylated phosphate esters, tristyryl phenyl ethoxylated phosphate esters and the like. Sodium dodecyl sulfate is preferred. The anionic surfactant is present in the amount of about 10-50%, preferably 20-45%, and most preferably, 25-35%, by weight.

The third component is a complexing agent which is characterized by being an organic compound having a

WO 98/49894 PCT/US98/05407

4

melting point of > 100°C., a molecular weight of ≤ 500, a water solubility of at least 10%, and being capable of hydrogen-bonding with the higher alkyl pyrrolidone. Suitable complexing agents for use herein have a dissociable proton which are present in hydroxy acids, such as lactic or citric acid; amino acids, such as glycine; sugars, such as lactose, sucrose, glucose or fructose; or amides, such as urea. The complexing agent is present in an amount of about 10-70%, preferably 30-60%, and most preferably, 25-50%, by weight.

Suitably a small amount of water is added to the mixture of components of (a), and the mixture is sprayed, freeze-dried or fluidized to form a solid.

Component (a) then is provided in the form of a free-flowing, high-melting solid, which is usually a granular, hydroscopic, or crystalline solid having a melting point of >100°C.

The (a) component then is admixed separately with (b), the SU, to form the desired SDS. Generally the SDS comprises about 80-99.5%, by weight, of (a) and 0.5-20% of (b), preferably 2-15%, and most preferably 3-10% of the SU. Optionally dispersant and/or wetting agents may be included in the SDS to assist in the formation of aqueous dispersions thereof upon dilution thereof with tank mix water. Optionally a hydrophobic polymer, or an inorganic mineral can be added to make the SDS less hydroscopic.

Typical active agricultural chemicals for use herein are shown below.

where X and Y are selected from the following:

6

X

Y

NAME

Bensulfuron methyl

Du Pont

Thifensulfuron methyl

Du Pont

Halosulfuron methyl

Nissan/ Monsanto

$$N$$
 CH_3

Prosulfuron

Ciba Geigy

Primisulfuron methyl

Ciba Geigy

OCHF2

Triasulfuron

Ciba Geigy

X

Y

NAME

OCH₃

WO 98/49894

8

Х

Y

NAME

$$CF_3$$
 N OCH_3 Flazasulfuron Ishihara OCH_3

Sulfonylurea herbicides are effective at very low doses, i.e. at a rate of application of only grams per acre. However, it is important to avoid an overdose during use. For this reason, sulfonylureas generally are used in combination with a diluent agchemical in an amount of about 20-50% by weight of the concentrate. Such diluent agchemicals usually have broad spectrum activity at a dosage rate of lbs per acre. Another advantage of using diluent agchemicals in the concentrate is that while sulfonylureas are available commercially only as solids, the diluent agchemical can be obtained in liquid form, e.g. as an emulsifiable concentrate. Accordingly, their admixture will provide a diluted liquid premix of the active for transport and use in preparing the stabilized liquid emulsifiable concentrate of the invention.

Some examples of diluent agchemicals for use herein include:

- (1) Phenoxy compounds:
- e.g. phenoxy acetates (MCPA esters), phenoxy
 propionates, and phenoxy butyrates (MCPB esters);
- (2) Benzoates (e.g. Dicamba);
- (3) Chloroacetamide/chloroacetanilides (e.g. Alachlor, Acetachlor, and Metolachlor);
- (4) Triazine derivatives (e.g. Metrubuzin), Triazinone (e.g. Metamitron);
- (5) Carbanilates (e.g. Phenmedipharm);
- (6) Thiocarbamates (e.g. Thibencarb); and
- (7) Phenylurea (e.g. Linuron and Diuron).

WHAT IS CLAIMED IS:

- A bioenhanced, stable solid carrier system for one or more sulfonyl or sulfamoyl urea active agricultural chemicals suitable for forming an aqueous microdispersed tank mix upon dilution with water, which comprises, by weight, (a) 80-99.5% of an inert matrix composition comprising 10-50% of a C₆-C₁₈ alkyl pyrrolidone, about 5-50% of an anionic surfactant and about 10-85% of a water-soluble, high melting organic compound containing a dissociable proton which can complex with said pyrrolidone, a melting point of > 100°C. a molecular weight of ≤ 500, and a water solubility of at least 10%, which is selected from the group consisting of hydroxy acids, amino acids, sugars and amides, and (b) 1-20% of said active agricultural chemical, optionally with a diluent agricultural chemical.
- 2. A system according to claim 1 wherein said diluent agricultural chemical is present.
- 3. A system according to claim 1 wherein (b) comprises about 0.5-20%.

- 4. A system according to claim 1 wherein (b) comprises about 1-10%.
- 5. A system according to claim 1 wherein the organic compound comprises about 20-75%.
- 6. A system according to claim 1 wherein the organic compound comprises about 25-50%.
- 7. A system according to claim 1 wherein the anionic surfactant comprises about 10-45%.
- 8. A system according to claim 1 wherein the anionic surfactant comprises about 20-35%.
- 9. An aqueous dispersion tank mix comprising the system of claim 1 and dilution water in an amount sufficient to reduce the concentration of the agriculturally active ingredient to between a few ppm and 1% by weight.
- 10. A method of making the system of claim 1 which comprises admixture (a) and (b) as separate components.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/05407

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) :A01N 25/02, 25/22 US CL : 504/116, 118, 211-217 According to International Patent Classification (IPC) or to both national classification and IPC						
	LDS SEARCHED					
Minimum d	documentation searched (classification system followe	d by classification symbols)				
U.S. :	504/116, 118, 211-217					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE, APS						
C. DOC	UMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.			
X,E	US 5,731,264 A (NARAYANAN et lines 25-39, col. 2, lines 1-39, and col	1-10				
Y	US 5,427,795 A (FEYEN et al.) 27 June col. 2, lines 1-44.	1-10				
Y,P	US 5,698,211 A (NARAYANAN) 16 30-55, col. 12, example 7.	1-10				
A	US 5,338,762 A (NARAYANAN) 16 A	1-10				
A	US 5,300,529 A (NARAYANAN) 05 A	1-10				
Y	US 5,230,892 A (FEYEN et al.) 27 Ju	1-10				
Further documents are listed in the continuation of Box C. See patent family annex.						
A Special categories of cited documents: "A* document defining the general state of the art which is not considered to the principle or theory underlying the invention						
E carlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is *X* document of particular relevance; considered novel or cannot be cons						
cit	ed to establish the publication date of another citation or other ecisi reason (as specified)	*Y* document of particular relevance; the				
me	seument referring to an oral disclosure, use, exhibition or other cans	considered to involve an inventive combined with one or more other such being obvious to a person skilled in the	documents, such combination			
"P" document published prior to the international filing date but later than "&" document member of the same patent family the priority date claimed						
Date of the actual completion of the international search Date of mailing of the international search report						
27 APRIL 1998		1 9 JUN 1998				
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT		Authorized officer S. MARK CLARDY				
Washington, D.C. 20231 Facsimile No. (703) 305-3230		Telephone No. (703) 308-1235				

Form PCT/ISA/210 (second sheet)(July 1992)*